

Growth from solutions: Kink dynamics, stoichiometry, face kinetics and stability in turbulent flow

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1. **Kink dynamics.** The first segment of a polygonized dislocation spiral step measured by AFM demonstrates up to 60% scattering in the critical length l^* — the length when the segment starts to propagate. On orthorhombic lysozyme, this length is shorter than that the observed interkink distance. Step energy from the critical segment length based on the Gibbs-Thomson law (GTL), $l^* = 2\omega\alpha/\Delta\mu$ is several times larger than the energy from 2D nucleation rate. Here ω is the building block specific volume, α is the step riser specific free energy, $\Delta\mu$ is the crystallization driving force. These new data support our earlier assumption that the classical Frenkel, Burton -Cabrera-Frank concept of the abundant kink supply by fluctuations is not applicable for strongly polygonized steps. Step rate measurements on brushite confirms that statement. This is the 1D nucleation of kinks that control step propagation. The GTL is valid only if $l^* < D_k/v_k$, the diffusion path of a kink that has diffusivity D_k and average growth velocity v_k . This is equivalent to supersaturations $\sigma < \sim a/2l^*$, where a is the building block size. For lysozyme, $\sigma \ll 10^{-2}$ (1%). Conventionally used interstep distance generated by screw dislocation, $19\omega\alpha/\Delta\mu$ should be replaced by the very different real one, $\sim 4l^*$.
2. **Stoichiometry.** Kink, and thus step and face rates of a non-Kossel complex molecular monocomponent or any binary, AB, lattice was found theoretically to be proportional to $1/(\xi^{1/2} + \xi^{-1/2})$, where $\xi \equiv [B]/[A]$ is the stoichiometry ratio in solution. The velocities reach maxima at $\xi = 1$. AFM studies of step rates on CaOxalate monohydrate (kidney stones) from aqueous solution was found to obey the law mentioned above. Generalization for more complex lattice will be discussed.
3. **Turbulence.** In agreement with theory, high precision in-situ laser interferometry of the (101) KDP crystal face shows step bunching if solution flows parallel to the step flow. The bunch height increases with the distance the bunch travels, i.e. with the face size. However, when the flow rate, u , increases, at $u > \sim 1$ m/s, the average step bunch height decreases as $1/u$. The phenomenon is attributed to the turbulent rather than laminar viscous boundary layer where diffusivity $D_t = 0.5u_\tau y$, i.e. increases linearly with the distance y from the solid face. Friction velocity, $u_\tau \sim u^{7/8}$. Dramatically larger rate of the mass/heat transport within the turbulent, as compared to the laminar, viscous layer will be discussed.